See Colour Plates 6, 7, 8, 9.

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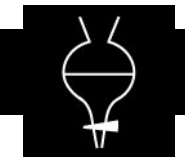
EXTRACTION



D. E. Raynie, The Procter & Gamble Company, Cincinnati, OH, USA

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Introduction

Extractions are common in the world around us. Each time we brew a cup of tea or a pot of coffee, and each time we launder our clothes, we're performing a chemical extraction process. Perhaps because of this familiarity, extraction processes in chemical laboratories are often not fully appreciated, or fully understood. Quite simply, an extraction is the process of moving one on more compounds from one phase to another. Yet behind this simple definition lies a great deal of subtlety: separations are contrary to thermodynamic intuition, because entropy is gained through mixing, not separation; extraction methods are developed based on a drive towards equilibrium, yet the kinetics of mass transfer cannot be ignored. Such a list of physical chemical nuances provides the basis for this chapter on the fundamentals of chemical extractions.

Extractions are carried out for a variety of reasons, for example when distillation is either impractical (e.g., distillations are favourable when the relative volatility of the compounds to be separated is greater than about 1.2) or is too expensive, to isolate material for characterization, to purify compounds for subsequent processing, etc. Extractions can be classified according to a number of schemes:

- analytical versus preparative (depending on the quantity of pure compound to be separated);
- batch versus continuous (depending on the mode of feeding the material to be separated into the extraction apparatus);
- based on the physical principles involved (is the extraction strictly based on partitioning, or are adsorption or other processes involved?);
- based on the types of phases involved (so called liquid–liquid extraction, gas–solid extraction, supercritical fluid extraction, etc.).

Perhaps the biggest recent advances in the field of chemical extractions have taken place in the petroleum, nuclear, and pharmaceutical industries. The understanding and practise of extraction lies at the crossroads of analytical, inorganic, organic, and physical chemistry, with theoretical and applied chemical engineering. Yet the fundamental physicochemical principles involved are the same. Because of the author's background, this chapter presents a description of the fundamental basis for chemical extractions and an overview of extraction techniques with a slant, or emphasis, towards the analytical chemists' perspective.

In general, the extraction process occurs as a series of steps. First the extracting phase is brought into intimate contact with the sample phase, usually by a diffusion process. Then the compound of interest partitions into or is solubilized by the extracting solvent. With liquid samples this step is generally not problematic. However with solid samples, for the compound being extracted to go into the extracting solvent the energy of interaction between the compound of interest and the sample substrate must be overcome. That is, the material's affinity for the extracting solvent must be greater than its affinity

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Table 1 Summary of selected extraction techniques by phases involved and the basis for separation

Extraction technique	*Sample phase*	*Extracting phase*	*Basis for separation*
Liquid–liquid extraction	Liquid	Liquid	Partitioning
Solid-phase extraction (and microextraction)	Gas, liquid	Liquid or solid stationary phase	Partitioning or adsorption
Leaching	Solid	Liquid	Partitioning
Soxhlet extraction	Solid	Liquid	Partitioning (with applied heat)
Sonication	Solid	Liquid	Partitioning (with applied ultrasound energy)
Accelerated solvent extraction	Solid	Liquid	Partitioning (with applied heat)
Microwave-assisted extraction	Solid	Liquid	Partitioning (with applied microwave irradiation)
Supercritical fluid extraction	Solid, liquid	Supercritical fluid	Partitioning (with applied heat)
Purge-and-trap	Solid, liquid	Gas	Partitioning
Thermal desorption	Solid, liquid	Gas	Partitioning (with applied heat)

for the sample. Finally the extracting phase (containing the compound of interest) must diffuse back through the sample, separate into a distinct phase, and be removed for subsequent processing. With proper selection of the extracting solvent this final step is generally not difficult, though the formation of emulsions must be avoided with liquid samples.

As previously mentioned, extractions (and other separation processes) are contrary to the principles of thermodynamics and work must be applied to overcome these thermodynamic constraints. Perhaps this has been expressed most eloquently by Giddings:

> It seems enigmatic that we often struggle so hard to achieve desired separations when the basic concept of moving one component away from another is inherently so simple. Much of the difficulty arises because separation flies in the face of the second law of thermodynamics. Entropy is gained in mixing, not in separation. Therefore it is the process of mixing that occurs spontaneously. To combat this and achieve separation, one must apply and manipulate external work and allow diffusion in a thermodynamically consistent way.

This external work is often applied as heat (temperature), which results in faster kinetics, decreased solvent viscosity and surface tension, increased solute solubility and diffusivity, and aids in overcoming interactions between the solute and the sample. A general analytical chemistry textbook (Peters, Hayes, and Hieftje (1974) *Chemical Separations and Measurements*: *Theory and Practice of Analytical Chemisty*. Philadelphia: Saunders) further describes the extraction process and areas for improvement:

> If two compounds are to be separated, we must, somewhere along the line, get them into two different and separable phases … At the heart of any chemical separation are the processes of (1) phase contact and equilibrium and (2) phase separation. These steps occur in all separation techniques, and a key in understanding a given method is the identification and classification of the steps according to the nature of the phases involved and the mechanism of phase contact and separation. Similarly, if a particular method of separation is to be improved, these are the only processes worth adjusting.

Using this discussion as a framework we can classify various extraction techniques according to the phases and applied work (or the basis of separation), as shown in **Table 1** for several selected extraction techniques.

The progress of an extraction is graphically depicted in **Figure 1**, which is a plot of the extraction yield (e.g. mass extracted) versus the progress of an extraction (e.g. solvent volume, time, equilibrium stages, etc.). This plot is generally asymptotic and consists of two regions. The initial, more steeply sloped region is the equilibrium region. This is the area where the effects of solute partitioning and solubility exist.

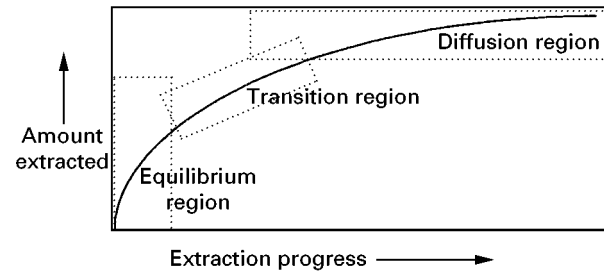

Figure 1 Plot of the relative amount (mass) extracted as a function of extraction progress (e.g. solvent volume, time, etc.). Three regions are defined: an equilibrium region dominated by solute partitioning, a diffusion region controlled by solute diffusion, and a transitional region.

As the extraction progresses it transitions into a region predominated by solute diffusion as well as the necessity for the solute to overcome effects such as solute–sample matrix interactions.

Preliminary Requirements

Chemical samples requiring extraction are composed of the compound of interest and the sample matrix, which may contain interfering species. Prior to choosing an extraction method, knowledge must be gained about the structure (including functional group arrangement), molecular mass, polarity, solubility, pK_a, and other physical properties of both the species of interest and potential interfering compounds. Constraints specific to the sample and the solvent must be considered, and the resulting concentration and desired degree of purification must be taken into account. This section discusses these preliminary considerations. Solvent-specific considerations and the roles of solute solubility, partitioning, and diffusion will subsequently be addressed.

Terminology

In discussing the fundamental processes in extraction, it is important to keep the appropriate terminology in mind. Extractions occur by the distribution of a compound between two immiscible phases. The mixture containing the component(s) to be separated is called the *feed* or *sample*. The extracted compounds of interest are described by several terms, including *solute* or *analyte*, while the phase left from the feed after being contacted by the extracting phase is the *raffinate* (generally used for liquids) or *residue* (solids). The *solvent* is the immiscible extracting fluid added to the process for the purpose of extracting solutes from the feed. One key feature is the lack of mutual solubility between the feed and the extracting solvent. Usually less than 10% solubility of the solvent in the feed is desired. Because phase separation is a defining parameter in chemical extractions, fluid flow is important for transporting the solute both through the sample (facilitating diffusional mass transfer by maintaining a concentration gradient at the interface between the phases) and through the system. Thus the solvent must be a gas, liquid, or supercritical fluid. (Solid extracting phases do not serve to move the extracted material through the system. In extraction techniques such as solid-phase extraction or matrix–solid-phase dispersion the solid phase assists in removing the solute from the feed, but fluid solvents are required to remove the solute from the solid phase.) During an extraction process, each equilibrium event is termed a *stage*; hence a theoretical (or equilibrium) stage is a mechanism, or extraction region, where the immiscible phases are brought under equilibrium conditions then physically separated. The placement of the extraction stage can help define the extraction process. For example, a *cross-current* extraction is composed of a cascading series of states where the raffinate is brought into a subsequent stage and contacted with fresh solvent. In a *countercurrent* extraction, the solvent and feed enter from opposite ends of the system, and these two immiscible phases pass each other in opposing streams.

Batch and Continuous Extraction Modes

One means of classifying extractions is based on the mode of operation, batch or continuous and static or dynamic. The terms batch and continuous refer to how the sample (feed) is placed into the system. In batch extraction processes the entire material to be extracted is loaded into the extraction device. In the case of continuous extractions the feed is continuously introduced into the extraction device. Static and dynamic describe the exposure of the two phases. In the static mode the extracting solvent and the feed are brought into contact and allowed to commingle for a prescribed period before the phases are separated, while dynamic extractions occur by continuously passing clean (whether fresh or recycled) extracting solvent through the sample.

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Most analytical extractions are performed using a batch-wise process. This mode is used when the distribution ratio (i.e., the ratio of the solute between the two phases) is high, favouring the extraction solvent. With batch extractions few stages are needed to achieve quantitative results, though phase separation has to occur before the extraction is complete. Batch extractions can occur in static or dynamic modes, or in some combination. For example, the familiar Soxhlet technique for extracting solid samples, depicted in **Figure 2**A, is considered a batch process with discontinuous solvent infusion, that is involving both static and dynamic modes.

Similar extractors for laboratory-scale liquid–liquid extraction, again shown in Figure 2, are also based on distilling the extracting solvent with subsequent condensation. The condensed solvent passes though the sample solution to be extracted, phase separation occurs, and the extracting solvent flows back into the receiving flask for redistillation. Design considerations account for the solvent density. The glassware shown in Figure 2B is representative of aqueous–organic extractions using heavier-than-water solvents, while Figure 2C illustrates an apparatus for use with lighter-than-water solvents.

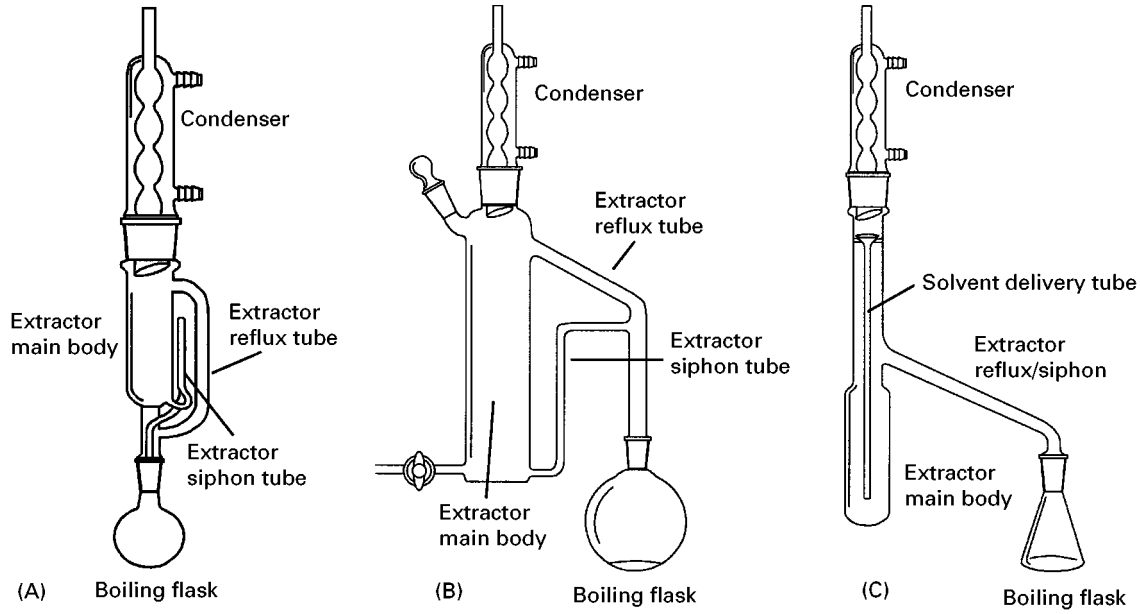

Figure 2 Laboratory glassware for performing (A) Soxhlet extraction, (B) liquid–liquid extraction with extracting solvents more dense than the liquid solvent, and (C) liquid–liquid extraction with extracting solvents less dense than the liquid sample.

When batch-wise extraction procedures are used for studying physical chemical properties, such as solubility or distribution ratios, special care must be taken, especially when aqueous phases are involved. Volume changes due to mutual solubility of the phases should be noted for precise measurements. Both the extraction and sampling must take place at the same temperature, since the values of many properties change as a function of temperature.

When distribution ratios are small, and also in many production-scale systems, continuous extraction processes are used. Continuous extractions are by definition also dynamic, since the two phases are continuously passed through each other. High efficiency continuous extractions depend on the viscosity of the two phases, the equilibrium rates, distribution ratios, solvent volumes, and the surface/contact area between the phases.

Countercurrent Extraction

A continuous extraction approach (though sometimes performed in a batch-wise manner) is countercurrent extraction. In countercurrent extraction both phases are continuously added (or changed) and flow in opposite directions as the extraction progresses. (When only one phase is continuously added, the procedure becomes a crosscurrent extraction.) In the case of both countercurrent and crosscurrent extractions, the feed is repeatedly (continuously) contacted or washed with extracting solvent. The number of theoretical stages is maximized by using solvents with favourable distribution coefficients (see subsequent discussion) or by increasing the solvent-to-feed ratio. Commonly, these processes employ up to eight theoretical stages. Although they have been replaced by chromatographic methods in many cases, countercurrent extractions are useful in that they use solvent only, without sorbents, and relatively mild conditions. They are favoured when the distribution coefficient is small. However, countercurrent extractions use large volumes of solvent and are not advantageous when large amounts of solute are to be isolated. The Craig countercurrent device, popularly used to study partition chromatography, is a discontinuous, differential migration process, since the extraction stages are performed step-wise rather than as continuous extractions.

Solvent Considerations

The requisite immiscibility and viscosity of the extracting fluid have been discussed.

Several other solvent properties that are important to the extraction process are listed here.

- Selectivity, i.e. the ability to extract the material of interest in preference to other, interfering material. Solvent selectivity can be supplemented through the use of adsorbents and secondary solvents, and by other means.
- High distribution coefficient to minimize the solvent-to-feed ratio.
- Solute solubility, which is usually related to polarity differences between the two phases, leading to low solubility in the raffinate.

- Ability to recover the extracted material. Thus the formation of emulsions and other deleterious events must be minimized.
- Capacity, the ability to load a high amount of solute per unit of solvent.
- Density, as density differentials are needed for countercurrent flow. The solvent density is related to solubility in supercritical fluid extracting solvents.
- Low interfacial tension to facilitate mass transfer across the phase boundary. Interfacial tension tends to decrease with increasing solute solubility and as solute concentration increases. In liquid–liquid extraction low interfacial tension allows the disruption of solvent droplets (entrained in the feed solution) with low agitation.
- Low relative toxicity.
- Nonreactive. In some instances, such as ion-exchange extractions, known reactivity in the extracting fluid is used. In addition to being nonreactive with the feed, the solvent should be nonreactive with the extraction system (e.g., noncorrosive) and should be stable.
- Inexpensive. Cost considerations should emphasize the energy costs of an extraction procedure, since, for a given extraction method, capital costs are relatively constant.

Solubility

Of the solvent properties necessary for extraction, solubility of the solute into the solvent is of fundamental importance. The general understanding of 'like dissolves like' is handy in the preliminary choice of extraction solvents. Solvent classification schemes are often helpful, especially if the selectivity of solvents is of interest. The Snyder selectivity triangle results in eight classifications of solvents according to proton donor, proton acceptor, and dipole interaction properties. Another solvent classification scheme is as follows.

- Class 1 solvents: capable of forming three-dimensional networks of strong hydrogen bonds.
- Class 2 solvents: have active hydrogen atoms and donor atoms, but do not form three-dimensional networks.
- Class 3 solvents: contain donor atoms, but not active hydrogen atoms.
- Class 4 solvents: contain active hydrogen atoms, but not donor atoms.
- Class 5 solvents: do not have hydrogen-bonding capability or donor atoms.

Comparisons of solubility values can give approximations for the partitioning of a solute between two solvents. Although experimentally generated solubility data is preferred, relative solubility scales can be used for estimation purposes. However, it is important to remember that no scale has been developed that completely accounts for all of the intermolecular interactions influencing solubility.

The most common relative solubility scale is the Hildebrand solubility parameter scale. The Hildebrand solubility parameter, δ, is a measure of the cohesion (interaction) energy of the solvent–solute mixture and is defined by $\delta = (\Delta E_v/V)^{1/2}$, where E_v is the heat (energy) of vaporization necessary for volume V. Thus, the ratio $\Delta E_v/V$ is the cohesive energy density. The 'total' Hildebrand solubility parameter (δ_t) is related to the hydrogen-bonding ability (δ_h), the dispersion coefficient (δ_d), and the polarity (δ_p) by $\delta_t^2 = \delta_h^2 + \delta_d^2 + \delta_p^2$. Consequently, there is a strong correlation between the Hildebrand solubility parameter value and the polarity. For extraction purposes, it is preferable to use solvents that have δ values similar to those of the solutes of interest. Several references provide detailed development of the Hildebrand solubility parameter, and similar scales, and these values are tabulated for several solvents.

When supercritical fluids are used in place of liquids, modified versions of the Hildebrand solubility parameter are used in which $\delta = 1.25P_c^{1/2}(\rho/\rho_{liq})$ or $\delta = \delta_{liq}(\rho/\rho_{liq})$, where P_c is the critical pressure, ρ is the density, and δ_{liq} and ρ_{liq} are the Hildebrand value and density at liquid conditions. This modification for supercritical fluids, while only approximate, provides for reference to liquid values of polarity and other 'chemical' properties, and for the relationship between supercritical density and solubility.

Solvent Removal Methods

Once the solute is extracted into the extraction solvent, it generally must be isolated from the solvent. Thus, the chosen solvent should facilitate this procedure. Most simply, this is done by evaporation or distillation of the solvent from the solute. Distillation procedures can be quite efficient. Other solvent removal methods include precipitation, adsorption, and back-extraction. Precipitation of the solute and subsequent decanting or filtering usually results in low yields. Where appropriate, these yields can be moderately improved by converting the (ionic) solute to the salt. Adsorption onto a suitable stationary phase is especially desirable if additional solute purification is needed. Back-extraction also results in additional purification. This secondary extraction can use a third solvent or can be an extraction back into the original feed solvent (for liquid systems) through changes in the distribution ratio by adjusting parameters such as pH. For example, with ionizable

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compounds and an aqueous phase the fraction ionized into the aqueous phase is approximated by the Henderson–Hasselbach equation (i.e., log ionized (α)/log nonionized $(1 - \alpha) = \text{pH} - \text{p}K_\alpha$). So in this example, the ionic form of 99% of the solute can be changed by adjusting the pH by two units from the $\text{p}K_\alpha$.

Extraction of Ions

The extraction of ionic species, especially from aqueous phases into organic phases, often requires somewhat specialized treatment, generally ion-exchange or ion-pairing extraction. In ion-exchange extraction the ionic compound is covalently bonded to a compound of opposite charge, resulting in a neutral species. The more common ion-pairing extraction is based on formation of a neutral ion pair through the interaction of the ionic species of interest with a counterion. The resulting neutral ion pair is soluble in organic solvents. Usually solubility is greater in polar solvents. The solubility in the organic solvent is usually increased by selecting an ion-pair reagent containing a nonpolar portion in addition to the charged moiety. Counterions used are generally soft acids or bases possessing large ionic radii. In addition to selection of the counterion, experimental parameters that can influence ion-pair extractions include pH, ionic strength (i.e., the total concentration of all ionic species in the sample), organic solvent, and flow rate.

Solute Distribution

Chemical extractions proceed by a drive towards equilibrium. Consequently, knowledge of the equilibrium distribution of the solute between the phases is useful. Berthelot and Jungfleisch studied phase distribution in 1871 and twenty years later, in 1891, Nernst developed his distribution law in which $K_\text{D} =$ (concentration of solute in phase1)/(concentration of solute in phase 2), where K_D is the *distribution coefficient*. However, the simple ratio of solute concentrations is not thermodynamically rigorous, since it does not account for association or dissociation in either phase. The IUPAC (International Union of Pure and Applied Chemistry) definition of the *distribution ratio*, K', includes all species of the same component and is used when the solute does not chemically react in either phase. This definition discusses the ratio, in organic–aqueous systems, as 'the total analytical concentration of the substance in the organic phase to its total analytical concentration in the aqueous phase, usually measured at equilibrium'. This relationship follows from Gibbs' phase rule in which: $P + V = C + 2$, where P is the number of phases, V is the number of degrees of freedom (independent system variables), and C is the number of components. So for the example of a simple extraction with two immiscible phases and a single solute of interest, $P = 2$ and $C = 3$. At constant temperature and pressure, the number of degrees of freedom is one, meaning the solute concentration in each phase is fixed. (Note that while activities and concentrations are not strictly equivalent, they can generally be treated equally over practical concentration ranges.)

Distribution ratios cannot be determined from the relative solubility data for several reasons: (1) the extraction may not be at equilibrium, (2) mutual solubility of the phases, and (3) solubility differences, for example between hydrated and anhydrous forms of the solute. Therefore the ratio of solubilities is not the same as the distribution ratio for these same reasons. However, if solvation is properly considered, the relationship between solubility and extractability can be determined, especially for liquid–liquid systems. Assuming equilibrium and phase immiscibility, the fraction of solute extracted, E, can be determined for a given phase ratio, V or V_1/V_2, by the expressions:

$$E = C_1V_1/(C_1V_1 + C_2V_2) = K_\text{D}V/(1 + K_\text{D}V)$$

$$E = 1 - [1/(1 + K_\text{D}V)]^n$$

$$\%E = 100K_\text{D}/(K_\text{D} + V_2/V_1)$$

where C is the solute concentration, n is the number of extractions (assuming the extracted phases are pooled), and subscripts 1 and 2 represent the two phases. A practical application of the use of distribution ratios is shown in **Figure 3**, which illustrates the need for a series of extraction stages, rather than simply, an increase in the volume of extraction

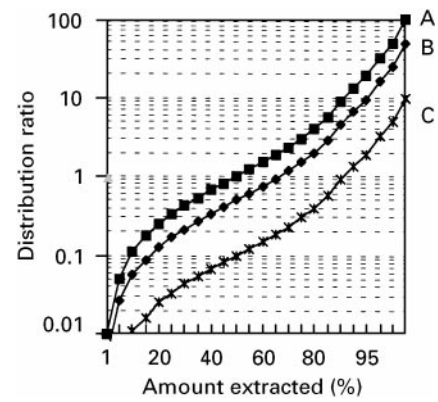

Figure 3 Relationship between distribution ratio and amount (percent) of solute extracted for (A) phase ratio of one, (B) phase ratio of two, and (C) phase ratio of ten.

Table 2 Solute distribution between phases in multistage extraction

	Stage				Distribution of solute
	0	1	2	3	
Initial equilibrated sample	a				
	b				
First transfer	0	a			
	b	0			
Amount of solute in each stage	a	b			$a + b$
Second transfer	0	ab	a^2		
	b^2	ba	0		
Amount of solute in each stage	b^2	$2ab$	a^2		$(a + b)^2$
Third transfer	0	ab^2	$2ba^2$	a^3	
	b^3	$2b^2a$	ba^2	0	
Amount of solute in each stage	b^3	$3b^2a$	$3a^2b$	a^3	$(a + b)^3$
Amount of solute in each stage upon subsequent transfers					$(a + b)^n$

solvent. In this example, assuming a constant distribution ratio of 1, a doubling of the extraction volume (from phase ratio = 1 to phase ratio = 2, where the phase ratio is the simple ratio of the extraction solvent volume to the sample volume) only increases the amount extracted in a single stage from about 50% to about 66%. A ten-fold increase in solvent volume only increases the amount extracted from about 50% to about 90%. As additional stages are added, the solute distributes itself in each phase. This is similar to the distribution studied by Craig and shown in **Table 2**. In this case, a solute distributes itself between the two phases in the ratio of a/b and the amount of solute in each stage can be determined. In practice, however, the stages are combined to maximize solute yield and recovery.

Diffusion

In addition to the roles of solubility and distribution ratios during the equilibrium portion of an extraction, diffusion is the largest factor influencing the extraction of solutes. Diffusion is that spontaneous, irreversible process by which a compound moves from an area of high concentration to an area of lower concentration, resulting in a concentration equilibrium within a single phase. More rigorously, the diffusional flow, J, of a compound is defined as the mass of the material of interest passing through a reference surface during a specified time, and laws of diffusion can correlate this diffusional flow with the concentration gradient responsible for the flow. If the rate of mass flow per unit area, or the diffusion flow, J, is in $g\,cm^{-2}\,s^{-1}$ and concentration is in $mol\,cm^{-3}$, Fick's first law of diffusion provides a correlation with the concentration gradient such that $J = -D(\Delta c/\Delta x)$, where D is the diffusion coefficient (given in $cm^2\,s^{-1}$) and $\Delta c/\Delta x$ is the concentration gradient (in $g\,cm^4$, concentration c is in $g\,cm^{-3}$ and area x is in cm^2). Thus, Fick's first law defines a diffusion coefficient that is independent of solute concentration and is unique to every solute–solvent pair at constant temperature. Generally, this diffusion coefficient, D, is in the range 10^{-5}–$10^{-6}\,cm^2\,s^{-1}$ in liquid solutions, whether aqueous or organic. When a steady state cannot be assumed, the concentration change with time must be considered, leading to Fick's second law of diffusion, $\Delta c/\Delta t = D(\Delta^2 c/\Delta x^2) = DV_{mol}^2 c$, where t is time (s) and V_{mol} is molar volume. Thus in non-steady-state conditions the temporal rate of concentration change is proportional to the spatial rate of concentration change in the direction of the concentration gradient.

Diffusion in Liquids

In liquid systems, with small or medium-sized molecules in dilute solution, diffusion is highly dependent on viscosity, η, and consequently on temperature, T. Assuming a spherical particle, diffusion in liquids can be expressed by the Stokes–Einstein equation, $D = (10^{-7}T/\eta V_{mol}^{1/3})$.

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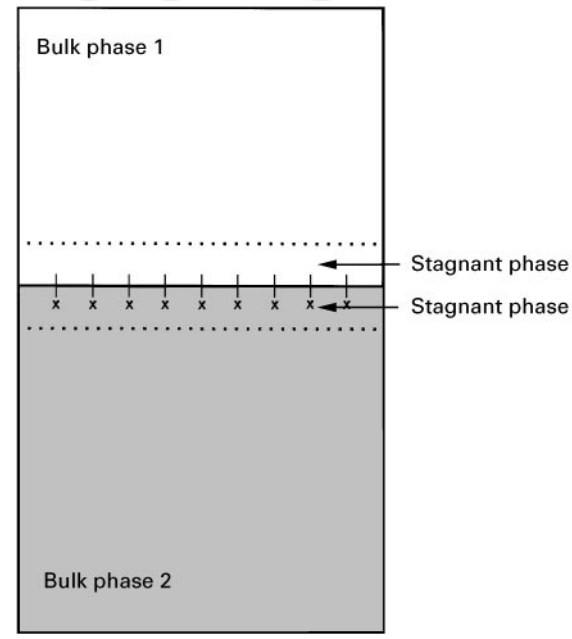

Figure 4 Schematic diagram of the role of interfacial diffusion in liquid–liquid extraction. Each stagnant layer is about 10^{-2}–10^{-4} cm. In this depiction, the molecules diffusing through the liquid–liquid interface contain a moiety (×) with an affinity toward phase 2 and a moiety (—) with an affinity toward phase 1.

For the purposes of extraction, the rate of diffusion across the liquid–liquid boundary layer is of primary importance. This diffusion rate is dependent on solute shape and size and on solvent viscosity. Agitation or turbulence at the liquid–liquid interface can enhance the rate of diffusion across the phase boundary, but there is a practical limit to the degree of agitation in an extraction mixture. **Figure 4** depicts the liquid–liquid system, including the stagnant films on either side of the phase boundary. In practical extraction examples the bulk phases are adequately stirred so that diffusion in the bulk phases can be neglected. However, the interfacial stagnant layers are about 10^{-2}–10^{-4} cm (compared with diffusion coefficients in the range 10^{-5}–10^{-6} $cm^2\,s^{-1}$) and must be considered as controlling the overall extraction kinetics. Moderate shaking or agitation can reduce the thickness of the stagnant, or stationary, films. If agitation is too vigorous, solutes in the mixture are given a high translational motion without an increase in the rate of solute movement to the phase interface. As phase dispersion increases, the relative velocity of the two phases decreases, until the limiting case of an emulsion (in which relative velocity becomes zero) is reached.

Diffusion in Solids

When extracting solutes from solid samples, one must not only overcome the solute–sample attraction, but the solute must diffuse with the solvent back out of the porous solid sample. This diffusion through the pores of a solid sample is influenced by the geometry or tortuosity of the pore structure (e.g. the diffusion path length). Diffusion in solids, assuming weak solute–sample sorption (i.e., a linear isotherm), is expressed by $D_{eff} = (\phi D)/\gamma(K_D + 1)$, where D_{eff} is the effective (or apparent) diffusivity), ϕ is the fraction of space available to the extracting solvent, K_D is the distribution coefficient (expressed as the ratio of solute concentration in the solid volume to solute concentration in the solvent volume), D is the (true) diffusivity in the bulk solvent, and γ is a tortuosity factor. With ionic solutes, if the pore wall carries an electric charge, diffusion is also affected by the electrical potential gradient.

This knowledge of diffusion through porous solids can provide an understanding of practical extractions. **Figure 5** represents an overview of the processes occurring when extracting solutes from solids. This understanding is described in the 'hot-ball model' advocated by Professors Keith Bartle and Tony Clifford at Leeds University. For example, with small quantities of extractable compounds that diffuse out of the homogeneous spherical particle into the extraction solvent, the extracted compounds are infinitely dilute. The extraction rate is obtained through the expression for the ratio of the mass, m, of

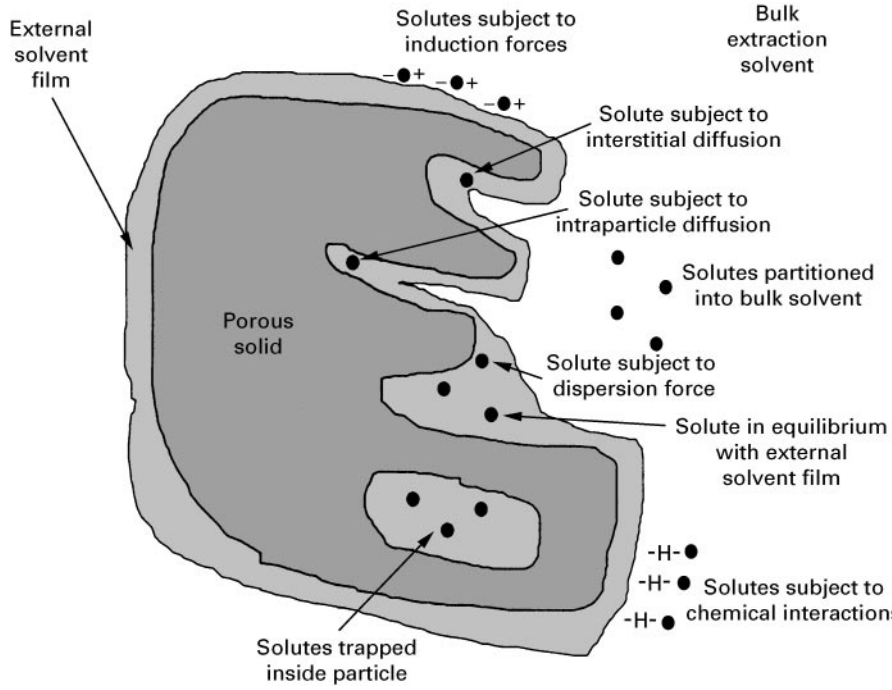
External solvent film
Solutes subject to induction forces
Bulk extraction solvent
Solute subject to interstitial diffusion
Solute subject to intraparticle diffusion
Solutes partitioned into bulk solvent
Porous solid
Solute subject to dispersion force
Solute in equilibrium with external solvent film
Solutes subject to chemical interactions
Solutes trapped inside particle

Figure 5 Schematic diagram of major physical/chemical processes that may occur during the extraction of solutes from a solid sample particle.

extractable material remaining after time t to the initial mass of extractable material, m_0, where $m/m_0 = (6/\pi^2)\Sigma(1/n^2)\exp(-n^2\pi^2 Dt/r^2)$, where n is an integer, D is the diffusion coefficient of the material in the sample matrix, and r is the radius of the spherical sample. This equation reduces to a sum of exponential decays, and a plot of ln (m/m_0) versus time eventually becomes linear. The physical explanation for the model is that, during the initial phases of an extraction, there is a concentration gradient at the surface of the sphere and diffusion from the sphere is rapid. This corresponds to the 'equilibrium' region (see Figure 1). When the concentration across the entire sphere becomes even and the rate of diffusion (and, hence, extraction) is a simple exponential decay, the 'diffusion' region of the extraction process (shown in Figure 1) is reached. Extrapolation of this linear portion of the plot of ln (m/m_0) versus time can be used to determine the time (or amount of solvent) necessary to achieve quantitative extraction recoveries.

Extraction Techniques

The previous sections described, in a practical way, the theory and the physical chemical basis for extraction. The importance of the phase interface was noted, and it was emphasized that mass transfer is a function of several properties, such as diffusion, viscosity, density, interfacial tension, turbulence, etc. Extractions are more practically a function of those experimental parameters that affect diffusion, viscosity, etc. For example, temperature plays one of the largest roles in improving extraction yields (though selectivity may suffer), as does the particle size of solid samples. The geometry of the extraction system must also be considered.

Chemical extractions can take on a number of embodiments. This section will provide a brief overview of these (mostly analytical) extraction techniques. The most important, and/or newly developed, are discussed in detail in other articles. While the methods discussed here are categorized as 'liquid' or 'solid' methods, there is some degree of exchange and methods used predominantly for solids can also be adopted for liquids in many cases, for example.

Extraction from Liquids

Liquid–liquid extraction (LLE) During LLE the solute partitions between two immiscible liquid phases. The devices shown in Figure 2, as well as the common separatory funnel, are simple laboratory methods for performing LLEs. The extraction solvents are chosen based on solubility differences with the sample solvent. For example, with neutral, acidic, or basic aqueous samples, organic solvents such as hydrocarbons, ethers, halocarbons, and aliphatic alcohols or ketones are commonly used. LLE can be performed in batch or continuous mode, can accommodate unattended operation, is suitable for systems with low distribution ratios, and uses relatively low solvent volumes. If solvent reflux is used care must be taken to avoid loss of volatile solutes and thermal degradation of the sample or the solute. In all LLEs the formation of emulsions should be avoided.

Solid–phase extraction (SPE) In SPE, a solid, or a liquid phase adhered onto a solid support, is used to selectively (and reversibly) retain sample components as the sample solution passes through the extraction device, usually configured as a packed bed or disk. The solute is then removed from ('washed off') the sorbent phase with the extracting solvent. In essence, this extraction procedure can be thought of as a crude chromatographic method and many of the same principles, and stationary phases, apply. SPE is especially useful for improving the selectivity of an extraction for instance to 'clean up' dirty samples for analysis. The selective stationary phases can retain solutes based on ionic or hydrogen bonding, or dipole–dipole, dipole–induced dipole, or dispersion forces. The primary advantages of the technique, in addition to selectivity, include speed, efficiency, reproducibility, economics, and safety.

Another, specialized, version of SPE is solid-phase microextraction (SPME). With SPME, the sorbent phase is coated on a small fibre which then comes in contact with the sample. The extracted solutes are eluted from the fibre, in most cases directly by the chromatographic inlet system. The advantage of this technique is that the extraction is coupled directly with the analytical chromatography (so that all of the solute is introduced into the chromatographic system) so that the system can be 'solvent-free'.

Extraction from Solids

It is estimated that 40% of all analytical samples are solids. This significant portion of the analytical sample load represents the most difficult extraction challenge, since solute interactions with the sample matrix must be overcome and the solute must then diffuse through the solid sample. As a result, the development of extraction methods for solids has focused on improving the diffusion issues.

Leaching Leaching simply involves soaking the sample in the extraction solvent for a prescribed period, and is a batch process. Because of the adsorp-

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tive properties of the sample and the slow diffusion through a solid, leaching is not a very efficient extraction method. Improvements to simple leaching can be made by placing the extraction vessel on a heat source (such as a heating plate or steam bath). Agitation, as in shake–filter methods, and a decrease in the sample particle size can also improve recoveries. An adaptation of leaching is forced-flow leaching. In this case the sample is placed in a tube and solvent flow is forced (under pressure) through the tube. In many instances the solvent is heated to near its boiling point and forced-flow leaching can be a continuous process.

Soxhlet extraction This common procedure, which uses the device shown in Figure 2A, was developed nearly 100 years ago and is still in routine use. The sample is placed into a porous container (called a thimble) and the volatile extraction solvent is continuously refluxed and condensed through the sample. Although the method can be slow (12–24 h Soxhlet methods are not uncommon), the apparatus can be left unattended with multiple extractions being performed by a bank of Soxhlet extractors. As with any technique using applied heat, loss of volatile compounds and thermal degradation are concerns. Because of its routine use in established analytical procedures, Soxhlet extraction is undoubtedly the extraction method to which other methods for extracting solids are compared.

New developments in Soxhlet extraction include a high pressure system, developed by J & W Scientific, which allows liquid carbon dioxide to be used as the extraction solvent, and an automated version. The automated Soxhlet extractor allows the thimble to be immersed in the boiling extraction solvent for a prescribed period, before the extraction is completed in the more traditional Soxhlet approach. This two-step process can be 4–10 times faster than conventional Soxhlet extractions and use about half of the solvent volume.

Sonication Sonication or ultrasound extractions can be considered a development of leaching, in which ultrasonic energy is applied to disrupt solute–sample interactions and facilitate solute diffusion. The use of ultrasonic probes can be quite efficient.

Accelerated solvent extraction (ASE) (also called pressurized fluid extraction) This technique, developed by the Dionex Corporation, is commonly discussed using the trademarked name, accelerated solvent extraction. However, the more generic term pressurized fluid extraction is becoming more widely used. In this technique the sample is placed into a sealed container and solvent is pumped through this extraction vessel. Because a modest pressure is applied, temperatures much greater than the atmospheric boiling point can be used with liquid extraction solvents. The technique is automated. This application of temperature greatly enhances solute solubility, diffusion, and viscosity, resulting in extractions that are qualitatively and quantitatively equivalent to Soxhlet in minutes instead of hours, and with significantly less solvent.

Microwave-assisted extractions In some respects microwave extractions can be thought of as a form of leaching with the addition of microwave irradiation. The microwave irradiation, when absorbed by materials with a permanent dipole, leads to heating. In a closed system, the approach is like ASE in the respect that temperatures greater than the atmospheric boiling point of the solvent can be achieved. This form of the technique is generally used with polar solvents (which absorb microwave energy). Open-cell approaches are generally used with non-absorbing solvents and samples with a high water content (or that otherwise possess a high dielectric constant). In this case localized heating in the sample allows extraction efficiencies to be improved.

Supercritical fluid extraction (SFE) SFE employs solvents, generally carbon dioxide (neat or with added co-solvents), at temperatures and pressures near or above the critical point. These high-temperature, high-pressure solvents have gas-like diffusion, liquid-like solvation properties, and do not possess surface tension. Hence, SFE can be quite rapid. With the use of carbon dioxide, the deleterious effects (e.g. cost, health and environment concerns, etc.) of organic solvents can be minimized. Another advantage of SFE is that solvating properties can be modified as a function of temperature and pressure, adding a selectivity advantage to the technique. In SFE the sample is placed in an extraction vessel and the supercritical fluid passes through the vessel in a series of static and dynamic steps. Upon depressurization of the extracting fluid the extracted solute remains in a solute collection region.

Gas-phase methods When volatile compounds are being extracted they can often be forced from the solid into the gas phase and subsequently trapped. In static methods the volatile compounds above the sample (often after heating) are simply trapped. Dynamic methods are exemplified by the purge-and-trap technique. In purge-and-trap, a continuous purge of the sample with an inert gas takes place and the volatile solutes are trapped onto a solid support. Thermal desorption is similar to the purge-and-trap technique, except the sample is heated ballistically to

higher, controlled temperatures to force the solutes into the gas phase. Each of these gas-phase methods have been modified for use with the SPME approach to solute trapping.

Future Directions

Chemical extractions are thought to be a mature science. However, progress is still being made. The key influences driving these advances include the need for faster and more selective extractions and extractions that use smaller (if any) amounts of organic solvents. Better predictive models to aid the design and scale-up of extraction processes will also continue to be of great interest.

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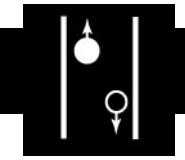
FLOTATION



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Introduction

Overview of the Essential Elements of Separations Based on Froth Flotation

The objective of a flotation separation operation is to remove small hydrophobic particles from an aqueous suspension (pulp) by causing them to collide with, and to attach to, air bubbles. The bubble–particle aggregates rise through the suspension forming a froth at the upper surface of the pulp. The froth, which consists of the bubble–particle aggregates with inter-bubble water containing both hydrophobic and hydrophilic particles, forms a second phase where further enhancement of the hydrophobic/hydrophilic particle separation occurs, by water draining back to the pulp. The final product in which the hydrophobic particles are concentrated is removed as a froth overflow.

The science of the separation is primarily concerned with improving the selectivity of the hydrophobic particle attachment in the pulp through the addition of surface active chemicals. In addition, the hydrodynamics of the bubble–particle collision in the aerated suspension is important, as is the regulation of the drainage of water-containing hydrophilic particles from the froth by controlling its structure, also with surfactants.

It is probably fair to say that the industrial practice of flotation is effective even in the absence of a complete understanding of its scientific basis. The successful application of flotation separations in industry can be classified into three areas.

Mineral Processing

Froth flotation is a widely used technique in the mineral processing industry as an early step in the process of concentrating a valuable material from an ore. It is preceded by crushing and grinding and may be followed by leaching/(ion exchange) electrowinning or smelting. In data cited by Merrill and Pennington from a US Bureau of Mines survey for 1960 nearly 200 million tons of raw material were processed annually by flotation in the USA from which 20 million tons of concentrates were recovered. These consisted of 34 different commodities which, although principally metallic and non-metallic ores and coal, also currently reflects an increasing interest in recycling waste material.

More recent data supplied by Bowes, courtesy of the Anglo-American Research Laboratories in Crown Mines South Africa, is given in **Table 1**. These figures are estimates and should be used with caution, as the